

Clarification of Water and Wastewater

BACKGROUND OF THE INVENTION

Field of the Invention

This application claims priority based on US continuation-in-part application, PCT Number US99/18338, U.S. serial number 09/140,203, filed August 12, 1998: and upon US continuation-in-part application serial number 09/343,616 filed on June 30, 1999. Both applications claim priority based on a parent application, US serial number 08/931,167, filed on September 16, 1997, now abandoned.

The parent application and the two continuation-in-part applications referenced above are herein incorporated by reference in their entirety. Providing, however: definitions and terminology established herein will govern the meaning of terms herein and below to the extent that there is any inconsistency.

In the following, the below definitions will be utilized:

Low molecular weight: 20K - 250K (20 to 250 cps @ 20% active in water and 40 to 1,000 cps @ 50% active in water)

Medium molecular weight: 500K - 1,000K (500 to 1,000 cps @ 20% active in water and 2,000 to 5,000 cps @ 50% active in water)

High molecular weight: 1000K - 5,000K (1,000 to 5,000 cps @ 20% active in water and >5,000 cps @ 50% active in water)

Very high molecular weight: > 5,000K (defined by individual intrinsic viscosity)

This invention relates to processes and improved processes for clarifying waters and wastewaters and for removing organic and inorganic contaminants from waters and wastewaters. In the examples below, aluminum polymers (AP) such as poly-aluminum hydroxychloride, poly-aluminum chloride, sulfated polyaluminum hydroxy chloride and poly-aluminum siloxane sulfate are combined with formulated medium, high and very high molecular weight ammonium polymers (AmP), such as di-allyl di-methyl ammonium chloride (DADMAC), epi-chlorohydrin di-methylamine (Epi-DMA) and polymers based upon amino-

methacrylate polyacrylamide chemistry, to significantly improve liquid-solid separation in waters and wastewaters.

5 *Sub. C2*
Aluminum polymer (AP) is used herein and below to refer to an aluminum polymer or polyaluminum composition such as aluminum chlorohydrate, aluminum hydroxychloride, polyaluminum chloride, polyaluminum hydroxysulfate, polyaluminum hydroxy chlorosulfate, polyaluminum chlorosulfate calcium chloride, a polyaluminum hydroxy "metal" chloride and/or sulfate, or a polyaluminum "metal" chloride and/or sulfate, and the like.

10 Medium, high or very high molecular weight AmP (M/H/VH MW AmP) can be medium or high molecular weight DADMAC, medium or high molecular weight Epi-DMA, and medium, high or very high molecular weight amino-methacrylated polyacrylamides. Very high molecular weight DADMAC and Epi-DMA do not exist at this time. Off-the-shelf cationic polyacrylamide is actually a VH MW AmP. It is reasonable to believe that an MMW and HMW polyacrylamide would perform similarly to the respective MMW and HMW DADMAC and Epi-DMA. An H/VH MW AmP should be understood below to include the very high molecular weight polyacrylamides together with the HMW AmP's. Medium molecular weights are included because those of skill in the art will realize, and limited tests indicate, that in some circumstances, in some raw waters, a medium molecular weight AmP will perform equivalently or nearly equivalently to a high molecular weight AmP. That is, the clarification result could meet industry standards.

15
20 The optimal HMW AmP choice in a given circumstance may depend on the chemistry of the waters or wastewater. The combination of AP and AmP may be further enhanced by blending the AP with an aluminum salt (AS). The AmP may be enhanced by blending with other medium, high or very high molecular weight AmP's and/or with low molecular weight quaternized ammonium polymers, such as DADMAC or Epi-DMA.

25 Due to the nature of water chemistry, as it is understood by those knowledgeable in the art, those known as water technologists, successful and optimal coagulants and/or chemical treatments for raw water and equipment combinations can only be determined by testing on the raw water. The industry established test is the jar test. The jar test is a reliable and established

method of determining an optimal and successful coagulant and/or chemical treatment when the test has been properly designed to match plant equipment constraints.

The invention herein disclosed is valuable for all raw waters. It should be understood, however, that not all possible individual combinations of AP and AmP (See Figure 9) for various illustrative CV products) would perform equally, optimally and/or as successfully in all raw waters. As individuals have individual fingerprints, raw waters are chemically unique in their respective contaminants, constituents and/or properties. Thus, water technologists know that testing is required to determine optimal and successful blends for different raw water and equipment combination.

The attached blend combinations of the CV 1700 and CV 1900 Series, listed in Figure 9, reveal different combinations for this chemistry. As one tests in different waters and follows the chemical and/or blending guidelines provided by this technology, one may determine other useful combinations that are not listed in Figure 9I yet are optimal and/or successful in a given raw water. These varying species are intended to be covered under the invention as disclosed herein.

~~Description of the Prior Art~~

In recent years, the problem of cleaning waters and disposing of wastewaters has become more acute due to increasing population and increasing industrial activity. Numerous solutions have been developed for treating raw waters. (The term "raw waters," which is used in the industry and is the technical term for describing waste-containing waters, is used hereafter to refer to any water or wastewater that requires treatment, including for example, industrial, agricultural, domestic and potable water.) One aspect of cleaning raw water is the separation of solids from liquids. Although separation practices have been known for hundreds of years, various new processes, devices and materials have been suggested during the past decades for the separation of solids from liquids in cleaning water.

Clarification units (or clarifiers), centrifuges and flotation units are among numerous devices that are used to provide liquid-solid separation. In general, clarifiers are used to separate inorganic and organic contaminants that are heavier than water (i.e., specific gravity >1.0) and flotation units separate contaminants lighter than water. A centrifuge may be

designed to remove either or both. In all cases, chemicals are added to the raw water to separate organic and inorganic contaminants from the raw water.

Two stages exist during water chemical treatment: coagulation and flocculation. Coagulation is the stage in water clarification when neutralized insoluble precipitates are formed upon addition of a coagulating agent such as an aluminum polymer (AP), or traditionally an iron salt or an AS. Coagulation is the stage where microfloculation begins. Final water quality is very dependent on the process of microfloculation. Flocculation is a stage in water clarification when the neutralized insoluble microfloculated precipitates are bridged and enmeshed into larger floc particles. Whether clarifiers or flotation units are used, a common feature of the raw water chemical treatment is a final stage in the chemical cleaning process when flocculation occurs. During flocculation contaminants that can be removed from the raw water are being aggregated into flocs that can be removed by settling or flotation prior to storage of the clarified water. If a filter is being used, flocs may accumulate on the filter. From time to time the filter must be washed or disposed of.

Flocs that settle in a bottom portion of a clarifier are removed from the bottom portion. Assuming floc settling velocity to be proportional to the square floc diameter (Stoke's Law of Liquid-Solid Separation), floc size can be a direct determinant of plant production capability.

It has been known to use anionic polyacrylamides as aides to "hold down clarifier beds" by creating a large floc. It has also been known to use anionic polyacrylamides as aides to cause flotation in combination with air. What is not believed to have been practiced before, however, is to add polyacrylamides with the AP's in the coagulation process.

In both clarifiers and flotation units, chemicals play an essential role. Aluminum salts (AS's), such as aluminum sulfate and aluminum chloride, have been used for decades as chemicals to clean water. In recent years, AP's, such as aluminum chlorohydrate, poly-aluminum chloride, sulfated polyaluminum hydroxy chloride and poly-aluminum siloxane sulfate, have also been used in chemical water treatment. Recently, the sulfated versions of aluminum polymers have been employed for cold temperature performance. However, while each of these AP's have the ability to clean water with a lower dosage than that required with AS's, these AP's create a very small floc as compared to that available with the AS's. Further,

microflocculation with AS's is determined by the available alkalinity. According to Stoke's Law of Liquid-Solid Separation, mentioned above, a small floc can present significant production restraints in water production equipment that is designed to separate the floc from the water.

5 Polymeric quaternized ammonium polymers (also known as ionene polymers or polyquats), containing chlorides or bromides as anions, have also been used for cleaning and clarification of raw waters. It is known that the usage of low molecular weight quaternized ammonium polymer can reduce the amount of aluminum salts or iron salts necessary to remove turbidity. In the past decade, blends of a low molecular weight quaternized ammonium polymer with an aluminum polymer have been formulated in order to enhance the efficiency of the aluminum polymer in the raw waters clarification process.

10 In addition, water alkalinity and water turbidity can play a role in the clarification of drinking waters. Performance of chemical sites that are formed for the microfloc formation during coagulation prior to a flocculation growth stage vary with alkalinity. These microfloc chemical sites are critical in the chemical cleaning of the water with iron salts or aluminum salts, as well as to a lesser extent with aluminum polymers. It is well known to a person skilled in the art of water treatment that significantly greater chemical dosages are typically needed for the clarification of water with low alkalinity than for the clarification of water with higher alkalinity. Pre-ozonation is known and used to assist salts in forming a microfloc. Pre-ozonation treatment can assist the formation of microfloc sites and lower the salt dosage.

15 Water having a "low alkalinity" will be used herein to refer to water with an alkalinity of less than 50 parts per million (ppm). Water having a "high alkalinity" will refer to water with alkalinity of greater than 100 ppm. Water having an alkalinity of greater than 50 ppm and less than 100 ppm will be referred to as "moderate alkalinity" water. The turbidity of a water refers to a waters solids concentration (on a weight basis). Low turbidity will be used herein to refer to an approximate turbidity of 20 NTU or less. "Moderate turbidity" waters will refer to a turbidity of greater than 20 and less than 150 NTU. High turbidity will refer to over 150 NTU (see Figure 1). While the chemicals specified in this invention are especially effective in low

turbidity waters, it is not intended that their use be so restricted. In fact, the instant chemicals are useful in a wide variety of raw waters.

High alkalinity waters have alkalinity levels that are high enough to fuel coagulation with salts under almost all operating conditions and may even require the plant to decrease (rather than increase) the alkalinity level. Moderate alkalinity waters contain enough alkalinity to allow a complete coagulation under most operating conditions. Low alkalinity waters have an alkalinity level that is so low as to limit the amount or type of a salt coagulant that can be added without the need to increase the alkalinity level. Thus, the low alkalinity waters are the most difficult to treat without having to resort to independently raising the alkalinity level. It is common for plants with individual turbidity units of less than 20 NTU, and preferably less than 10 NTU, and alkalinity values less than 30 ppm to add clay and/or lime to the water to facilitate the chemical cleaning operation. Clay and/or lime is then removed with any accumulated floc and disposed. The lower the turbidity in the low alkalinity waters, still more difficult is the chemical treatment.

For the very difficult to treat low alkalinity, low turbidity waters, medium, high and very high molecular weight AmP's have been discovered to be especially effective in fueling the coagulation process. In low alkalinity raw waters with moderate and high turbidity, the medium, high and very high molecular weight AmP's have also been discovered to be especially effective in both fueling coagulation and beginning to remove turbidity particles. As the turbidity of the raw water increases, the medium, high and very high molecular weight AmP's have been discovered to be especially effective in primarily removing turbidity particles so that the aluminum compounds can be more effective and the M/H/VH MW AmP play a minor role in fueling the coagulation. In high alkalinity water that has low turbidity, it has been discovered that medium, high and very high molecular weight ammonium polymers still enhance AP performance but are required in much lower percentages to fuel coagulation for optimal performance.

High alkalinity, low turbidity water is clarified most easily. Since the water alkalinity is high, the alkalinity itself helps fuel the coagulation process. Meanwhile, since the turbidity is low, much less water cleaning is required than for moderate and high turbidity waters. The

aluminum compounds alone normally perform satisfactorily and sometimes achieve the required government standards. While the technology of the instant invention will out perform the aluminum compounds alone in high alkalinity low turbidity raw waters, this improvement is usually in cost of operation rather than in water quality performance. However, it has been found that this technology can eliminate the need for pre-chlorination or pre-ozonation. Therefore, for treatment of raw waters that have a TOC greater than 2.0 mg/L, this technology can minimize the formation of disinfection by-products during coagulation and flocculation.

In addition, final water pH is an important parameter in drinking water units as low pH water can present a bad taste to many individuals. Final water pH targets are normally between 7.5 and 9.0. Traditionally, the chemical cleaning process is performed with a salt of aluminum or of iron. Therefore, the pH is normally lowered by the salt in the raw waters during chemical cleaning to keep the cations available. Often, the water pH is reduced to the 4.5 to 5.5 range. Low pH water will deteriorate operating equipment over time. Raising the pH back to the 7.5 to 9.0 range requires the addition of either caustic or lime at considerable expense. The process of salt addition followed by caustic and/or lime addition increases plant operating costs. The salt and lime precipitates must be removed from the water either in clarification or in filtration. Removal is costly. Salt and lime precipitates form a small floc, termed pin-floc, that must be removed by filtration. This pin-floc significantly reduces filter run time "hours" increasing operating expense. Also, salt and lime precipitates settle in the clarifier or flotation unit or centrifuge creating a hydroxide sludge that is high in water content. Most salt and salt/lime sludges are 99% water. This sludge can be a significant operating cost as this sludge must be disposed of.

When poly-aluminum hydroxychloride ($Al_xOH_yCl_z$ or its similar chemistries) react to chemically clean raw water, hydroxyl groups are released into the raw waters. Chemical treatment with AP in general normally maintains or slightly increases the raw water pH. Therefore, treatment with AP can save costs due to a reduction in the amount of either caustic or lime required to raise the pH. However, the smaller floc size of AP can be a limiting factor to the successful application of AP. It has been discovered that proper use of AmP along with

AP can result in improved final water quality with a reduction in overall operation costs, taking into account cost savings for pH corrections, filter hours and sludge disposal.

Many patents related to water treatment are mostly specialized and particularly protect a limited area. For example, some patents are solely oriented towards removal of organic (but not inorganic) contaminants from water. (Pohl, U.S. Patent No. 5,262,059, issued on November 16, 1993, patents a method of removing organic contaminants from raw waters that contain an undesired liquid organic contaminant such as an organic solvent. Box, Jr. et al, U.S. Patent No. 4,268,399, issued on May 19, 1981, patent a process for purification of organically polluted water using a zinc titanate catalyst under oxidizing conditions. McCarthy et al, U.S. Patent No. 4,115,264, issued on September 19, 1978, patent a method of purifying organically polluted water containing negligible amounts of alkali metal by contacting the polluted water with an oxygen-containing gas and a catalyst effective to promote such liquid phase oxidation. Box, Jr. et al, U.S. Patent No. 3,823,088, issued on July 9, 1974, patent a method of purifying organically polluted water by contacting the polluted water with a catalyst comprising zinc aluminate promoted with at least one metal active for initiating oxidative reactions in the liquid or gaseous phase under oxidizing conditions. Ritter, U.S. Patent No. 5,474,703, issued on December 12, 1995, described a method for clarifying bodies of water and eliminating algal bloom caused by planktonic algae using a flocculating agent prepared in an aqueous solution containing a combination of monomeric or polymeric aluminum salts and a polybasic carboxylic acid.

Hassick, et al, U.S. Patent No. 4,746,457, issued on May 24, 1988, described the use of aluminum chloride/water soluble cationic polymer compositions having inorganic polymer activity ratios of at least 5:1 and preferably 20:1 to 100:1. Hassick et al, U.S. Patent No. 4,800,039, issued on January 24, 1989, described the use of poly-aluminum hydroxychloride/water soluble cationic polymer compositions having inorganic:polymer ratios of at least 5:1 and preferably 20:1 for clarifying waters with low turbidity and moderate and high alkalinity. Kvant et al., U.S. Patent No. 5,182,094, issued on January 26, 1993, claimed a process for the preparation of polyaluminum hydroxide complexes using aluminum

compounds. Figures 10 and 11 illustrate comparison testing against Hassick's inventive teachings.

The above-listed patents and many other similar inventions have been developed, some patents of which still exist in the market. Although many different issues have been solved by these previously- and presently-existing purification and clarification processes and materials, there still remains room for improvement in the area of clarification of raw waters for industrial and municipal purposes. There remains a need for improved materials and processes for the separation of solids from raw waters.

The timing of the instant invention is significant since presently the USEPA is requiring a lowering of drinking water final turbidity targets (i.e., turbidity of filtered water), thus requiring a lowering of drinking water turbidity targets after clarification prior to filtration, as well as after filtration. Traditionally, filtered water turbidity targets were 0.5 NTU and settled water turbidity targets were 5.0 NTU. In 1999, the new standards for the turbidity of filtered water are 0.3 NTU, with 0.1 NTU to be achieved in 3 to 5 years as indicated in pp. 100-101, Section 7.3.1 of the 1998 Edition of the EPA Handbook, entitled "Optimizing Water Treatment Plant Performance Using the Composite Correction Program," which provides required government regulations for water treatment. The filtered water turbidity target of 0.1 NTU corresponds to a settled water turbidity target of 1.0 NTU. In many instances the traditional salt and polymer technology does not provide a chemical capability or an economical chemical pathway to water production for a filtered water turbidity of 0.1 NTU.

The new NTU targets are being set to provide consumers with drinking water that is sufficiently free of microbial pathogens to prevent waterborne diseases. During the past 20 years, the most common suspected causes of waterborne disease outbreaks were the protozoan parasites *Giardia lamblia* and *Cryptosporidium parvum* as stated in Safe Drinking Water Regulations, Federal Register, 63 FR 69477-69521, published on December 16, 1998, referred to as "SDWR". *Giardia* and *Cryptosporidium* may cause extended illnesses, sometimes lasting months or longer, in otherwise healthy individuals (SDWR, p. 9 of 85). Potential annual benefits that can be gained by removing *Cryptosporidium* from drinking water are shown in SDWR, p. 49 of 85. Although disinfection requirements have been developed for inactivation

of Giardia cysts, inactivation of Cryptosporidium is currently being investigated by the water industry and research institutes. EPA has a particular concern regarding drinking water exposure to Cryptosporidium, because there is no effective therapeutic drug to cure the disease. (SDWR p. 10 of 85). As of February 16, 1999, the government has established regulations (referred to as the Interim Enhanced Surface Water Treatment Rule (IESWTR)) regarding the new requirements for maximal resulting turbidity of settled water and filtered water in order to improve control of microbial pathogens, particularly Cryptosporidium. The IESWTR applies to public water systems that use surface water or ground water under the direct influence of surface water (GWUDI). (SDWR, p. 2 of 85). Pilot study work showed that when treatment conditions were optimized for turbidity and particle removal, very effective removal of both Cryptosporidium and Giardia was observed (EPA Handbook, p. 9). Under the conditions tested in the pilot study work, meeting a filter effluent turbidity (i.e., filtered water turbidity) of 0.1 NTU (which corresponds to settled water turbidity of 1.0 NTU) was indicative of treatment performance producing the most effective cyst and oocyst removal (EPA Handbook, p. 9). Another pilot study and full-scale plant work demonstrated that consistent removal rates of Giardia and Cryptosporidium were achieved when the treatment plant was producing filtered water of consistently low turbidity (0.1 - 0.2 NTU), as stated in EPA Handbook, p. 9. Pilot study work has shown that a small difference in filtered water turbidity (from 0.1 NTU or less to between 0.1 and 0.3 NTU), produces a large difference in cyst and oocyst removal. (EPA Handbook, p. 9). In addition, filter plant performance evaluations conducted at filtration plants have shown that when filter effluent turbidity was less than or equal to 0.2 NTU, 60% of plants were given an acceptable rating (versus 11% at 0.3 NTU), once more indicating the benefit of lowering filtered water (and, thus, settled water) turbidity (EPA Handbook, p. 10). Therefore, an extensive amount of research and field work results support a filtered water maximum turbidity goal of 0.1 NTU (and, thus, a settled water maximum turbidity goal of 1.0 NTU). Based on such test results and regulations, the required settled water turbidity is aimed to be 0.1 NTU and the present invention is based upon such goals.

In addition, five years ago, there were no demands for water production facilities for either color or Total Organic Carbon (TOC) removal and there were no limits on the soluble

aluminum concentration remaining in the filtered water. Removal of color and TOC from raw water containing organics historically has been accomplished by either pretreatment or enhanced treatment with chlorine, by treatment with Granular Activated Carbon (GAC) or by overtreatment with aluminum. Recently, removal of color and TOC has been accomplished with ozonation.

Pretreatment or enhanced treatment of the raw water with chlorine creates disinfection by-products, tri-halo-methanes (THM) being one group which are known cancer causing chemicals. Another group of disinfection by-products, halo-acetic acids (HAA's) are known birth defect forming chemicals. Until recently, many water treatment plants were still pre-chlorinating. At the present, there are THM and HAA regulations that nearly eliminate pre-chlorination activities, as stated on p. 15 of 146 of National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts, Federal Register, 63 FR 69389-69476, published on December 16, 1998, referred to as "NPDWR". The maximum contaminant level goal(MCLG) of THM or HAA is 0.06 ppm, i.e., 60 ppb. To stay within allowable THM and HAA guidelines (60 ppb), water production facilities have stopped pre-chlorination and only perform post-clarifier/pre-filter or post-filter chlorination. Therefore, the capability of improving settled water and filtered water turbidities, TOC and color removal by pre-chlorination has been effectively outlawed by default.

Treatment with GAC is very expensive.

Treatment with ozone is very expensive. Very recently, ozonation has been scrutinized for formation of a new type of disinfection byproduct, aldehydes and ketones.

In addition, overtreatment with alum leads to the existence of soluble aluminum in the final water product. Aluminum is linked to Alzheimer's Disease. Therefore, limits of 0.2 ppm aluminum content are being imposed as stated in "CH-290 Water Hygiene," published by the Texas Natural Resource Conservation Commission ("TNRCC"), 02/04/99, pp.29-30. The limit of 0.2 ppm aluminum content is applicable to all public water systems. Application of such limits effectively eliminates overtreatment with aluminum as an option in water clarification systems.

In the IESWTR, the government requires that all public water systems using conventional filtration, regardless of size, are to be filtered sufficiently to remove specified percentages of organic materials (measured as TOC) that may react with disinfectants to form disinfection byproducts (p. 15 of 146 of WPDWR). Removal of such specified percentages of organic materials, without using chlorine, GAC, or alum can be achieved through treatment techniques that also enhance coagulation and softening.

Based on the government regulations, certain removal percentages of TOC by the enhanced coagulation and softening of raw waters have been established. The required removal percentages of TOC depend upon the raw water TOC and alkalinity, as demonstrated in PCT Figure 2.

Systems practicing enhanced (lime and/or caustic) softening must meet the TOC removal requirements of the last column on the right. Since THM and HAA concentrations are directly related to water TOC, the lower the resulting TOC, the lower is the resulting THM or HAA concentrations. The long term goal of the guidelines is to reduce TOC to less than 2.0 mg/L. Specific ultraviolet absorbance (SUVA) is an indicator of the treatability of disinfection byproducts precursors that can be removed. SUVA is defined as the UV-254 measurement (measured in m^{-1}), divided by the dissolved organic carbon (DOC) concentration (measured in mg/L or ppm). DOC is the dissolved portion of TOC. Insoluble organic carbon (IOC) is the insoluble portion of the TOC, being equal to the TOC-DOC.

Meanwhile, a maximum color content for settled and filtered water is established by the government (as stated on p. 30 of CH-290 Water Hygiene). A color content of at most 15 standard color units in filtered water must be achieved.

From different angles and different directions, a conclusion is reached that the lower the turbidity, the color content, the aluminum content and the TOC of the settled water, the healthier is the filtered water. Based on such facts, the government has presently imposed: a required filtered water turbidity goal of 0.3 NTU and is presently aiming towards establishing a required filtered water turbidity goal of 0.1 NTU, TOC removal guidelines, final THM and HAA concentrations, along with maximum aluminum concentrations.

SUMMARY OF THE INVENTION

Int. C3

A primary object of the invention is to devise an effective, efficient and economically-feasible process for separating solids from raw waters, such that the treated waters meet or exceed local, state and/or federal guidelines.

5 A further object of the invention is to devise an economically-feasible process for treating raw waters containing organic and/or inorganic contaminants.

A further object of this invention is to devise an efficient and effective chemical process of coagulation that does not require pre-oxidative treatment, thereby the formation of disinfection byproducts are eliminated in coagulation.

10 Yet another object of this invention is to devise a process for treating raw waters that requires a minimum amount of treatment chemicals.

15 Still another object of this invention is to devise a process for treating raw waters with low alkalinity and low, moderate and high turbidity, with moderate alkalinity and low, moderate and high turbidity, and with high alkalinity and low, moderate and high turbidity to achieve a settled water turbidity of 1.0 NTU.

An additional object of this invention is to devise a process for treating raw waters, such that equipment investment operating cost and operating capital that are needed in the treatment process are minimized.

20 A yet further object of this invention is to provide a process for treating raw waters, such that reduction of color content, turbidity, total organic carbon and aluminum content are enhanced and simplified.

Additional objects and advantages of the invention will be set forth in part in a detailed description which follows, and in part will be obvious from the description, or may be learned by practice of the invention.

25 The present invention provides a process for chemical treatment of water and wastewaters (referred to throughout the application as "raw waters") to achieve clarification. Effective amounts of aluminum polymers (AP's) (defined above as an aluminum polymer or polyaluminum composition such as aluminum chlorohydrate, aluminum hydroxychloride, polyaluminum chloride, polyaluminum hydroxysulfate, polyaluminum hydroxy chlorosulfate,

polyaluminum chlorosulfate calcium chloride, any polyaluminum hydroxy "metal" chloride and/or sulfate, any polyaluminum "metal" chloride and/or sulfate and the like) and possibly aluminum salts (AS's), such as alum, aluminum chloride and the like are combined with medium, high and very high molecular weight ammonium polymers such as diallyl dimethyl ammonium chloride (DADMAC), epichlorohydrin di-methyl amine (Epi-DMA) and the like as well as cationic and non-ionic polyacrylamides, either prior to storage at a water production facility or during a chemical cleaning process of the water production facility, to clarify the raw waters and to substantially reduce, and even often remove, any organic and inorganic contaminants. As defined herein the medium molecular weight ammonium polymer (AmP) has a molecular weight of greater than approximately 500,000 and less than 1,000,000 as measured by having a viscosity greater than about 500 and less than 1,000 cps at a concentration of approximately 20% in water. High molecular weight AmP is defined as 1,000,000 to 5,000,000 molecular weight measured as 1,000 to 5,000 cps at a concentration of approximately 20% in water. Very high molecular weight AmP's are defined as greater than 5,000,000 molecular weight measured as greater than 5,000 cps at a concentration of 20% in water and specifically measured by their intrinsic viscosity. Low molecular weight AmP has a molecular weight ranging from 20,000 to less than 250,000 as measured by having a viscosity of 20 to 250 cps at a concentration of approximately 20% in water. Since Epi-DMA's are normally 50% active, low molecular weight Epi-DMA has a molecular weight ranging from 20,000 to less than 250,000 as measured by having a viscosity of 40 to 1,000 cps at a concentration of approximately 50% in water. Further, medium molecular weight Epi-DMA can be correlated to have a molecular weight ranging from 500,000 to 1,000,000 (as measured by having a viscosity of 2000 to 5000 cps at a concentration of 50% in water) and 1 million to 5 million (as measured by having a viscosity of about 1,000 cps to about 5,000 cps at a concentration of approximately 20% in water). Polyacrylamides may be cationic, non-ionic or anionic, the selection further depending on the quality of the raw water. Cationic polyacrylamides are preferably quaternized, but not necessarily so. Anionic polyacrylamides should be added separately.

Preferred cationic monomers for polyacrylamides are dialkylaminoalkyl (meth) - acrylates and -acrylamides, generally as acid addition or quaternary ammonium salts, and diallyl dialkyl ammonium halides. The preferred acrylates and methacrylates are preferably di-C₁₋₄ alkylaminoethyl (meth) acrylates and the preferred acrylamides are di-C₁₋₄ alkylaminopropyl (meth) acrylamides, in particular dimethylaminoethyl (meth) acrylate and dimethylaminopropyl (meth) acrylamide (with the respective acrylate and the respective acrylate and methacrylamide compounds being particularly preferred) as acid addition and quaternary ammonium salts. For most purposes the most suitable cationic monomer is a diallyl dialkyl quaternary salt, preferably dimethyl ammonium chloride. Generally a single cationic monomer is used, but if desired a copolymer may be formed, for instance from diallyl dimethyl ammonium chloride and dimethylaminopropyl methacrylamide salt, generally with the latter in a minor proportion.

Instead of forming the coagulant polymer by addition polymerization of ethylenically unsaturated monomers, any other known ionic coagulant polymers can be used. For instance suitable polymers are polyethylene imine and polyamines, e.g., as made by condensation of epichlorhydrin with an amine. Other polymers include aminomethylolated polyacrylamide (free base or quaternary or acid salt), poly (acryloxyethyltrimethylammonium chloride), poly (2-hydroxypropyl-1-N-methylammonium chloride), poly (2-hydroxy-propyl-1, 1-N-dimethylammonium chloride), poly (acryloyloxyethyl diethylmethyl ammonium chloride and poly (2-vinylimidazolium bisulfate). Mannich polymers may be used; however, stability is normally a concern.

The present invention further provides a process for turbidity reduction that combines AP's or AP's in combination with AS's with medium, high or very high molecular weight AmP's. Polyacrylamides are to be added along with the other components as part of the coagulation stage. Polyacrylamides are preferably a part of a blend in combination with AP or AP with AS. The process may be further enhanced by adding low molecular weight DADMAC and/or low molecular weight Epi-DMA. The addition of aluminum chloride can provide enhanced color and TOC reduction, while the addition of low molecular weight Epi-DMA and/or low molecular weight DADMAC can increase the effectiveness of the aluminum polymers at turbidity reduction. Blends of medium or high or very high molecular weight

AmP's and low molecular weight DADMAC and/or low molecular weight Epi-DMA with at least one aluminum salt and/or at least one aluminum polymer have provided satisfactory results.

The invention also relates to methods of blending and storing preferred AP and AmP chemicals.

It is to be understood that the descriptions of this invention are exemplary and explanatory, but are not restrictive, of the invention. Other objects and advantages of this invention will become apparent from the following specification and from any accompanying charts, tables and examples.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph demonstrating ranges of alkalinity and turbidity that are covered in this invention.

Figure 2 demonstrates the relationship between removal percentages of TOC relative to raw water TOC and alkalinity.

Figure 3 shows test results for water of low alkalinity with low turbidity.

Figure 4 shows test results for raw water of low alkalinity and moderate to high turbidity.

Figure 5 shows test results for raw water of low alkalinity with low to high turbidity.

Figure 6 shows test results for raw water of moderate to high alkalinity and moderate to high turbidity.

Figure 7 shows test results for raw water of moderate to high alkalinity with low turbidity.

Figure 8 shows comparison test results.

Figure 9 shows the constituents of certain combinations of chemicals used for jar tests.

Figures 10 and 11 show comparison results.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Preferred embodiments of the present invention are illustrated in any charts, tables, drawings and examples that are included.

The present invention provides a process for chemically treating raw waters to achieve clarification. The process that is presented significantly improves liquid-solid separation equipment processes that presently exist in the market, including improving turbidity results. The invention is also directed towards the removal of at least the IOC content of any organic matter from raw waters, thereby decreasing the TOC. The process can also result in a filtered water with less than 0.2 mg/L aluminum content, color less than 5 standard units, and minimize the need for ozonation.

The process for clarification of raw waters by chemical treatment is focused on application of at least one of a medium or a high or a very high molecular weight ammonium polymer (AmP) in combination with aluminum polymers (AP's) or AP's in concert with aluminum salts (AS's) to treat the water.

In one embodiment, the clarification process comprises blending in the raw water or adding to the raw water AP or AP and AS with at least one high or very high molecular weight AmP to form a flocculated suspension.

This invention uses various chemical combinations to significantly improve liquid-solid separation in raw waters. (To simplify the description of the present invention, "separation" would implement complete or significant separation.)

In the prior art, blends of DADMAC or polyquaternary amines such as epichlorohydrin dimethyl amine (Epi-DMA), having a low molecular weight, with aluminum salts or aluminum chlorohydrate has been applied. In the instant invention blends of the materials always include a significant fraction of AmP of a higher molecular weigh range, thereby providing a system that cleans raw waters much more efficiently and effectively. Traditionally, DADMAC's were sold at a molecular weight from about 50,000 to about 700,000 which correlates to a viscosity in the range of about 50 cps to about 700 cps at a concentration of abut 20% in water. Improved water cleaning and flocculation performance is herein observed upon using DADMAC having a molecular weight of at least about 500,000 and preferred 1,000,000 to about 5,000,000, with a 20% active product, at viscosities of about 500 cps and preferred 1,000 cps to 5,000 cps.

Vinyl polymers having water solubility and cationic characteristics, as described above, include modified polyacrylamides, modification being made, for example, by the typical

Mannich reaction products or the quaternized Mannich reaction products known to the art, or other vinylic polymers which use as a vinyl monomer those monomers containing functional groups which have cationic character. As an example, but not meant to be limiting on this invention, we include in these types of vinyl monomers such monomers as AETAC, APTAC, DMAEM, DMAEM DMS quat., DACHA HC1, DADMAC, DMAEA, MAPTAC, METAMS, AMPIQ, DEAEA, DEAEM, MAEAcAm, DMAEMAcAm, DEAEcAm, DEAEMAcAm, and ALA, the quaternized compounds containing the polymers, polymers containing diallyldimethylammonium chloride monomer, and the like. To be effective these additive polymers, be they condensation polymers or vinyl polymers, must have a medium, high or very high molecular weight. A preferred polymer is a condensation polymers derived from the reaction of epichlorohydrin and dimethylamine.

AETAC	=	Methacroyloxyethyltrimethyl ammonium chloride
APTAC	=	Acryloyloxyethyltrimethyl ammonium chloride
DMAEM	=	Dimethylaminoethylmethacrylate
DMAEM DMS quat.	=	Dimethylaminoethylmethacrylate quaternized with dimethyl sulfate
DACHA HC1	=	Diallylcyclohexylaminehydrochloride
DADMAC	=	Diallyldimethylammonium chloride
DMAEA	=	Dimethyl aminoethyl acrylate and/or its acid salts
MAPTC	=	Acrylamidopropyltrimethyl ammonium chloride
METAMS	=	Methacrylamidopropyltrimethyl ammonium chloride
AMPIQ	=	1-acrylamido-4-methyl piperazine (quaternized with MeCl, MeBr, or Dimethyl Sulfate)
DEAEA	=	Diethylaminoethylacrylate and/or its acid salts
DEAEM	=	Dimethylaminoethylmethacrylate and/or its acid salts
DMAEAcAm	=	Dimethylaminoethylacrylamide and/or its acid salts
DMAEMAcAm	=	Dimethylaminoethylmethacrylamide and/or its acid salts
DEAEAcAm	=	Diethylaminoethylacrylamide and/or its acid salts
DEAEMAcAm	=	Diethylaminoethylmethacrylamide and/or its acid salts

ALA = Allyl amine

Aluminum Polymer is used herein to refer to an aluminum polymer or polyaluminum composition such as aluminum chlorohydrate, aluminum hydroxychloride, polyaluminum chloride, polyaluminum hydroxysulfate, polyaluminum hydroxy chlorosulfate, polyaluminum chlorosulfate calcium chloride, a polyaluminum hydroxy "metal" chloride and/or sulfate, a polyaluminum "metal" chloride and/or sulfate and the like. The aluminum polymers include the sulfated versions of aluminum polymers. Optionally the aluminum polymers can be blended in the raw water or added to the raw water individually or with an aluminum salt such as an alum or an aluminum chloride and the like. At least one high or very high molecular weight AmP is added to or blended in the raw water. If desired, the high or very high molecular weight can be added with a low molecular weight Epi-DMA and/or with a low molecular weight DADMAC.

Blends of the medium or high or very high molecular weight AmP's (including of course the polyacrylamides) with AmP's and/or AS's in the present invention are aimed at significantly improving the coagulation and the flocculation capability of the chemical compounds. The present invention discloses blends of a medium or high or very high molecular weight AmP with at least one AP or an AP/AS combination to have provided satisfactory results, even for raw unclarified water with alkalinity of less than 50 ppm while simultaneously causing the removal of algae from the raw water. A preferred embodiment of the AmP's is a blend of a medium or high molecular weight DADMAC, Epi-DMA and/or a high or very high molecular weight polyacrylamide with aluminum chlorohydrate ($Al_xOH_yCl_z$). Blends of medium or high molecular weight DADMAC and/or Epi-DMA with ($Al_xOH_yCl_z$) and/or AS have also been successfully applied. Blends of medium or high molecular weight DADMAC and/or Epi-DMA and/or medium, high or very high molecular weight polyacrylamides with $Al_xOH_yCl_z$ and/or AS provide a system that cleans many raw waters much more efficiently and effectively than existing systems while simultaneously causing the removal of algae from the raw water. Improved water cleaning and flocculation performance is normally observed with a 20% active product, at viscosities greater than, 500 cps. A 20% active product at viscosities greater than 1,000 cps is preferred. Blends of the high molecular weight and/or very high MW

AmP with aluminum chloride have also provided acceptable results for raw unclarified waters with alkalinity of less than 50 ppm. A preferred embodiment is a blend of high molecular weight DADMAC or Epi-DMA and/or high or very high molecular weight polyacrylamide with aluminum chloride. In prior art, blends of aluminum chloride with polyquaternary amines, such as Epi-DMA, have been applied with low molecular weight Epi-DMA, or molecular weight units of about 2,000 to 150,000. Blends of the present application include a higher molecular weight range of Epi-DMA and provide a system that cleans raw waters much more efficiently and effectively.

Further, blends of at least one medium, high and/or very high molecular weight AmP with at least one low molecular weight quaternized ammonium polymer and with at least one AS and/or at least one AP have provided acceptable results while simultaneously causing the removal of algae from the raw water. A preferred embodiment is a blend of a high molecular weight DADMAC or Epi-DMA and/or high or very high molecular weight polyacrylamide with at least one AS and/or at least one AP. The AS's are preferably alums, aluminum chlorides or any combinations thereof.

With embodiments of the present invention it has been discovered that color units, turbidity units, TOC, disinfection byproducts and aluminum content are lowered more easily and more efficiently. There is improved coagulation and an increase in the size of flocs, resulting in cleaner water along with higher rates of floc settlement than rates available for flocs using the lower molecular weights AmP's. The increase in coagulation and in the floc size is particularly significant when the high molecular weight and/or very high molecular weight AmP is used in combination with AP's in low alkalinity and low turbidity water.

With embodiments of the present invention, it has been discovered that there is a reduced dosage of inorganic chemicals that are required to clean the raw waters, in particular to comply with new standards of settled turbidity, TOC, disinfection byproducts and residual soluble aluminum. In the case of AS's or AP's, the reduction can be in the rate of about 30 percent to about 90 percent. The reduced overall dosage of the inorganic chemical can be a determinative factor in the application of the AP's, since AP's generally are much more expensive and create a very small floc in comparison flocs created by aluminum or iron salts.

Even when resulting turbidity is not significantly reduced with embodiments of the present invention, dosage and operating cost may be significantly reduced.

The required amount of pH adjustment is significantly reduced with embodiments of the instant invention. Traditionally, either caustic or lime is used to accomplish this raise of final water pH in drinking water plants. The process of salt addition followed by caustic and/or lime addition increases plant operating costs. The salt and lime precipitates must be removed from the water either in clarification or in filtration. Removal is costly. Salt and lime precipitates form a small floc, termed pin-floc, that must be removed by filtration. This pin-floc significantly reduces filter run time "hours" increasing operating expense. Also, salt and lime precipitates settle in the clarifier or flotation unit or centrifuge creating a hydroxide sludge that is high in water content. Most salt and salt/lime sludges are 99% water. This sludge can be a significant operating cost as this sludge must be disposed of. Since the higher molecular weight AmP's reduce the required amounts of aluminum salt and allow the application of AP's, use of the higher molecular weight AmP's can present significant cost savings to water plants.

In combination with AP's, the higher molecular weight AmP's present significant potential chemical cost savings in the clarification of low alkalinity water. Medium, high and/or very high molecular weight AmP's are able to provide sites of micro-flocculation, achieving flocculation despite insufficient alkalinity and turbidity of the raw water. Thus, there is a reduction in the amount of chemicals needed for cleaning low alkalinity water with the higher molecular weight AmP's in combination with AP's (versus aluminum salts or aluminum salts in combination with low molecular weight quaternized ammonium polymers).

Since pre-ozonation is done to assist aluminum and iron salts to perform microflocculation, the use of high and/or very high MW AmP's in combination with AP or AP and AS can eliminate the need for pre-ozonation, thereby significantly reducing the need for ozonation in general, further reducing costs and eliminating the disinfection byproducts of ozonation.

Medium, high and/or very high molecular weight AmP's make a larger floc at lower dosages than low molecular weight quaternized ammonium polymers do. Formation of larger flocs at lower dosages is particularly beneficial in oil/water separation as would normally be

accomplished in a flotation unit. By using medium or high molecular weight DADMAC and medium or high molecular weight Epi-DMA, raw waters are clarified and algae are removed.

Algae are also removed during clarification of water upon applying a high or very high AmP, preferably high molecular weight DADMAC, and a herbicide. The present invention can be applied under a variety of conditions and in many different apparatus.

Blending these multi-component chemical systems is an important criterion to most users of this technology as most users of this technology either will not have the equipment for multiple chemical feed systems and/or will not be interested in controlling a multi-component chemical feed system. While prior blending is not required, prior blending is preferred.

Previous art either has been unable to blend or has had significant limitations on the blending of these chemicals. It has been generally accepted in the industry that:

1. Dry cationic and dry non-ionic polyacrylamides could not be blended with AP's and/or AS's and/or solution polymers such as DADMAC and Epi-DMA as the inclusion of dry polymers resulted in a lumping of the polyacrylamide known as "Fish Eyes." This inhibition has reduced the previous combination of these chemicals to the utilization of either the emulsion form of polyacrylamides, which are only 40 to 60 percent active in a hydrocarbon solvent, or to a costly step of effecting a combination of solution polymers, such as AP's or DADMAC or Epi-DMA, during a polyacrylamide emulsion finishing process.

2. AP's and/or AS's could not be blended with DADMAC unless the catalyst for DADMAC manufacture was sodium persulfate. It was accepted that DADMAC manufactured with ammonium persulfate could not be blended with AP's as the aluminum would precipitate from solution over a relatively short period of time.

3. AS's and/or AP's were difficult to blend with either Epi-DMA and/or DADMAC.

4. AP's and AS's could not be blended together or together could not be blended with polyacrylamides, DADMAC and/or Epi-DMA.

Notwithstanding the above, it has been found that stable blends of these chemistries can be manufactured, preferably in accordance with the below guidelines:

- The basicity of the final solution when blending aluminum chloride solution with $Al_xOH_yCl_z$ is maintained less than 55% and preferably less than 45% for stability.
- Termination of the Epi-DMA reaction is accomplished with an acid other than acids containing sulfur, such as sulfuric and sulfurous acid. Reactions terminated with hydrochloric acid are preferred. Subsequent blending of Epi-DMA terminated with HCl has shown excellent results when the other blending guidelines mentioned herein are followed.
- DADMAC can be manufactured with either sodium persulfate or ammonium persulfate when the other blending guidelines mentioned herein are followed.
- All AmP's, AP's, AS's and any dilution water are preferably blended in the following order:
 1. Blend water and required solution polymers,
 2. Perform pH adjustment, preferably with hydrochloric acid or with any acid with an anion compatible with AP, such as HBr, etc. (Sulfur containing acids will lead to aluminum precipitation.) pH adjustment should be less than 6.0 and is preferably 4.25 +/- 0.25 to match the pH of the AP.
 3. Blend any required AP after pH adjustment.
 4. Any required aluminum salt is added after AP.
 5. Required cationic or non-ionic polyacrylamides are added last.
- Aluminum containing chemical(s) is preferably added in combination with high shear mixing.
- Any required cationic or non-ionic polyacrylamide is added in combination with high shear mixing at the point of addition followed by slow mixing. Final solution viscosity is significantly affected by the addition of polyacrylamide; therefore, it is preferred to only add dry polyacrylamides to concentrations of 3% or less and emulsion polyacrylamides to concentrations of 8% or less.

- Once the aluminum chemical(s) is added, the addition of any basic or oxidation material is preferably avoided as addition may lead to aluminum precipitation.
- Anions containing sulfur are preferably minimized or eliminated from any blend containing AP unless those anions are included during the manufacturing process of AP.
- The use of any sulfated AP may eliminate the use of any aluminum salts.
- Any required anionic polyacrylamide should be added separately at the point of use.

Numerous tests have been performed on the clarification process. Optimizing the clarification process has been a common goal of all the tests. The results of some of the tests run for enhancing clarification of the raw waters follow.

EXAMPLE 1

In the water production facility of Bonham, Texas, aluminum sulfate, a low molecular weight DADMAC and bentonite clay are used to produce water with a turbidity ranging from about 0.1 NTU to about 0.3 NTU. The alkalinity normally is between about 10 ppm to about 20 ppm. The raw turbidity usually ranges from about 3 NTU to about 6 NTU. The chemical dosages are normally from about 40 ppm to about 60 ppm alum, about 10 ppm bentonite clay and about 20 ppm low molecular weight DADMAC.

Jar tests were performed with a poly-aluminum chloride/aluminum chlorohydrate blend of Applicant (being 50% active) and high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), producing water with a turbidity of about 0.7 NTU without any filtration. The chemical dosages were approximately 12 ppm by volume (12 ppm x 1.36 specific gravity x 0.5 concentration = 8.2 ppm by weight) of the 50% active poly-aluminum chloride/aluminum chlorohydrate blend and approximately 2.5 ppm by volume (2.5 ppm x 1.04 specific gravity x 0.2 concentration = 0.5 ppm by weight) of the 20% active high molecular weight DADMAC, with the weight ratio of the poly-aluminum chloride/aluminum chlorohydrate blend to high molecular weight DADMAC being 8.2 ppm:0.5 ppm = 16.4.

EXAMPLE 2

In the water production facility of Camden, Arkansas, ferric sulfate is used to produce water with a turbidity of approximately 0.1 NTU. The alkalinity is normally near 10 ppm. The raw turbidity usually ranges between about 5 to about 20 (with a turbidity of less than 20 NTU being referred to as "low turbidity" and a turbidity of greater than 20 NTU being referred to as a "moderate turbidity" herein). Chemical dosages are normally about 30 ppm to about 60 ppm iron sulfate.

Jar tests were performed with a poly-aluminum chloride/aluminum chlorohydrate blend of Applicant (being 50%) active and high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), producing water with a turbidity at approximately 0.1 NTU without any filtration. Dosages were about 6 ppm by volume ($6 \text{ ppm} \times 1.36 \text{ specific gravity} \times 0.5 \text{ concentration} = 4.1 \text{ ppm by weight}$) of the 50% active poly-aluminum chloride/aluminum chlorohydrate blend and about 2.5 ppm by volume ($2.5 \text{ ppm} \times 1.04 \text{ specific gravity} \times 0.2 \text{ concentration} = 0.5 \text{ ppm by weight}$) of the 20% active high molecular weight DADMAC, with the weight ratio of the poly-aluminum chloride/aluminum chlorohydrate blend to higher molecular weight DADMAC being $4.1 \text{ ppm} : 0.5 \text{ ppm} = 8.2$.

Jar testing with the iron sulfate required approximately 40 ppm iron sulfate. Without using any filtration, water with a turbidity of about 1.5 NTU was recovered. Later, plant production testing revealed final water of 0.023 NTU with 7 ppm of the 50% active aluminum polymer blend and 2.0 ppm of the 20% active high molecular weight DADMAC.

EXAMPLE 3

In the water production facility of Antlers, Oklahoma, aluminum sulfate is used alone to produce water having a turbidity ranging from about 0.1 NTU to about 0.3 NTU. The alkalinity is normally less than 10 ppm. The raw turbidity normally is between about 3 NTU to about 10 NTU. The chemical dosage of alum normally ranges between about 40 ppm to about 60 ppm.

Jar tests were performed with a poly-aluminum chloride/aluminum chlorohydrate blend of Applicant (being 50% active) and high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), producing water with a turbidity of approximately 0.6 NTU without any filtration. The dosage of the poly-aluminum chloride/aluminum chlorohydrate blend was about 8 ppm by volume (8 ppm x 1.36 specific gravity x 0.5 concentration = 5.4 ppm by weight) and of the high molecular weight DADMAC was about 2.5 ppm by volume (2.5 ppm x 1.04 specific gravity x 0.2 concentration = 0.5 ppm by weight). The weight ratio was 5.4/0.5=10.8.

Jar testing with the aluminum sulfate required approximately 40 ppm by weight aluminum sulfate and, without using any filtration, water with a turbidity of 1.0 NTU was recovered.

EXAMPLE 4

In the water production facility of Greenville, Texas, aluminum sulfate and a typically-used low molecular weight DADMAC are used to produce water of a turbidity of less than 0.1 NTU. The alkalinity normally ranges from about 10 ppm to about 30 ppm. The raw turbidity normally is between about 3 NTU to about 10 NTU. Chemical dosages are normally from about 40ppm to about 60ppm alum and about 2 ppm of the low molecular weight DADMAC.

Jar tests were performed with poly-aluminum chloride/aluminum chlorohydrate blend of Applicant (being 50% active) and high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), producing water with a turbidity at approximately 0.4 NTU without any filtration. The dosage of the poly-aluminum chloride/aluminum chlorohydrate blend was about 8 ppm by volume (8 ppm x 1.36 specific gravity x 0.5 concentration = 5.4 ppm by weight) and of the high molecular weight DADMAC was about 2.5 ppm by volume (2.5 ppm x 1.04 specific gravity x 0.2 concentration = 0.5 ppm by weight), with the weight ratio of poly-aluminum chloride/aluminum chlorohydrate blend to high molecular weight DADMAC being 5.4 ppm/0.5 ppm = 10.8.

Jar testing with aluminum sulfate required approximately 60 ppm aluminum sulfate and approximately 2 ppm of DADMAC and, without using filtration, water with a turbidity of

approximately 0.8 NTU was recovered. In jar testing with aluminum sulfate, water pH was reduced to 6.1, while jar testing with poly-aluminum chloride/aluminum chlorohydrate blend and high molecular weight DADMAC raised water pH from 6.6 to 7.1.

EXAMPLE 5

Formosa Plastics in Point Comfort, Texas, produces about 4 to 5 million gallons per day of wastewater. In the first stage of the wastewater treatment process, dissolved air flotation units are employed to remove oils at the surface and inorganic solids are removed by rake in the bottom of these units.

A low molecular weight DADMAC, blended with aluminum chlorohydrate had been in use having a turbidity/total suspended solids (NTU/TSS) removal efficiency in a range of between approximately 40 percent to approximately 50 percent. The low molecular weight DADMAC blend as added to the dissolved air flotation unit at a dosage of about 6 ppm to about 8 ppm. An anionic flocculant was added in a dosage ranging from about 1.0 ppm to about 1.5 ppm.

Fifty percent active aluminum chlorohydrate in a 60% ratio (referred to as CV 1120) and 20% active high molecular weight DADMAC in a 40% ratio of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), were added to the dissolved air flotation unit at concentrations ranging from about 4 ppm to about 6 ppm in concert with an anionic flocculant ranging between approximately 1.0 ppm and approximately 1.5 ppm. This product increased the dissolved air flotation unit efficiency to over about 70 percent.

EXAMPLE 6

In DeQueen, Arkansas, alum is used in a final clarifier to remove algae prior to wastewater discharge. Removal of total suspended solids (TSS) is a critical discharge parameter, as with all wastewater treatment facilities. The dosage of alum typically ranges from about 100 ppm to about 250 ppm. Adding approximately 3 ppm to 5 ppm of CV 3650 (high

molecular weight DADMAC) causes a reduction of the required alum to less than 100 ppm, while keeping the total suspended solids less than 15 ppm.

Waste aluminum chloride (being 18% active and being obtained from a styrene production facility of Dow Chemical) was blended with high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), in a ratio of 65:35. At dosages about 35 ppm and about 40 ppm of the blend, the plant was in permit at 6 ppm total suspended solids. (Permit is 15 ppm total suspended solids). Alum (obtained from 48% active liquid of General Chemical) alone required in excess of 200 ppm and said alum in combination with CV 3650 required 90 ppm by volume alum/4ppm by volume CV 3650, respectively.

EXAMPLE 7

In Beaumont, Texas, alum is used in a French Pulsation Clarification System. Typical values are between 20 ppm and 25 ppm of raw alkalinity, 8 ppm of calcium, raw water turbidity units (NTU) of 40 to 60 and raw color of 40 to 80 units. Alum usage is normally 45 to 55 ppm at raw color units of 40 to 60. An anionic polyacrylamide is used in emulsion form at a dosage of 0.2 to 0.4 ppm to control pin floc carryover and floc size. As the raw color units rise, the alum usage increases such that at raw color units of 120 the alum usage is 90 to 100 ppm. The city of Beaumont normally utilizes 30 to 40 ppm of 50% caustic for pH adjustment, along with 55 ppm of caustic to pH adjust the alum sludge which would otherwise corrode the sewer line.

The optimal chemistry for Beaumont as performed in numerous jar tests is a combination of aluminum chlorohydrate of Applicant (referred to as CV 1120 and being 50% active), high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), low molecular weight Epi-DMA of Applicant (referred to as CV 3210 and being 50% active) and aluminum chloride (referred to as CV 1135 and being 10% active) in combination with the anionic polyacrylamide. Utilizing this chemistry, dosages of 12 to 14 ppm obtained a final filtered NTU of 0.08 along with 1 color unit. Plant operation with and jar tests with alum revealed final NTU's of 0.22 at

55 ppm. pH adjustments with alum required 32 ppm of 50% caustic where this chemistry only required 8 ppm.

Further, the higher pH values capable with this chemistry allows for the removal of manganese and taste and odor from the raw water with potassium permanganate and chlorine dioxide. Neither of these chemicals can perform with alum as the low pH value for alum removes their oxidation potential.

EXAMPLE 8

In Marshall, Texas alum was used in a sedimentation basin system. Typical values are between 20 ppm and 25 ppm of raw alkalinity, 12 ppm of calcium, raw water turbidity units (NTU) of 5 to 8 and raw color of 40 to 200 units. Alum usage is normally 32 to 38 ppm. During periods of 200 raw color units, the city cannot maintain turbidity targets of 0.3 NTU or less. Augmentation of the alum with 1 ppm to 2 ppm of high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), reduces final NTU's to less than 0.1 and allows the plant to stay in permit. Prior to usage of CV 3650, the plant went out of permit with high color raw water.

Jar tests with a combination of aluminum chlorohydrate of Applicant (referred to as CV 1120 and being 50% active), high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), low molecular weight Epi-DMA of Applicant (referred to as CV 3210 and being 50% active) and aluminum chloride (referred to as CV 1135 and being 10% active) produced a settled 0.7 NTU at a dosage of 8 ppm. This compares favorably to 32 ppm alum and 2 ppm of CV 3650 obtaining 0.6 NTU in the same test.

EXAMPLE 9

In Longview, Texas, alum is used in a sedimentation basin system. Typical values are between 20 ppm and 25 ppm of raw alkalinity, 10 ppm of calcium and raw water turbidity units (NTU) of 1 to 3. Alum usage is normally 18 to 25 ppm. Settled NTU is normally 1 to 1.5. Final NTU is normally 0.15 to 0.20.

5 The chemistry for Longview performed in numerous jar tests is a combination of aluminum chlorohydrate of Applicant (referred to as CV 1120 and being 50% active), high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active), low molecular weight Epi-DMA of Applicant (referred to as CV 3210 and being 50% active) and high molecular weight Epi-DMA of Applicant (referred to as CV 3250 and being 50% active). This combination at dosages of 3 to 4 ppm produces 0.17 NTU settled/filtered in a jar test while alum at 18 ppm produced 0.16 NTU. The alum required a 300 percent increase in lime to pH adjust as compared to this new chemistry.

10 EXAMPLE 10

15 In Nederland, Texas, PRC 3050C is used in a solids contact clarification system. Typical raw alkalinity values are between 0 ppm and 30 ppm. Polymer usage is very dependent on the raw color which can vary from 20 to over 300. Polymer usage varies from about 15 ppm to over 70 ppm. Final NTU is normally less than 0.10.

20 The optimal chemistry for Nederland as performed in numerous jar tests is a combination of aluminum chlorohydrate of Applicant (referred to as CV 1120 and being 50% active) and high molecular weight of DADMAC of Applicant (Referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active). This combination produced 0.6 NTU water at 10 ppm beside the current system that produced 0.8 NTU at 16 ppm, on the day tested. Testing with tannic acid found the new chemistry to significantly remove more color than the PRC 3050C. Raw water testing from the Neches River Upstream of Nederland found that water spiked with tannic acid to 120 color units had a removal to 14 color units with this chemistry while the current system only obtained 32 color units.

25 EXAMPLE 11

In Omaha, Nebraska, a cold lime softening system is used to clarify high turbidity water from the Missouri River. Pretreatment is normally done with a typical DADMAC (having a molecular weight near 200,000 and being 20% active producing 200 cps). Usage of the high

molecular weight DADMAC reduced operating dosages by over 70% while producing water at less than 0.1 NTU. The DADMAC is also used as a filter aid at this facility.

Further, at Omaha, to meet competitive bidding requirements, high molecular weight DADMAC of Applicant (referred to as CV 3670, having a molecular weight greater than 1 million and being 10% active) was delivered as 10% active at viscosities of 150 to 250 cps. The previous low molecular weight version was 20% active at 200 cps. At only 10% activity, the CV 3670 still outperformed the low molecular weight version by 25 to 30 percent in dosage.

EXAMPLE 12

In Hugo, Oklahoma, aluminum chlorohydrate is used in a reactor clarification system. Typical raw alkalinity values are 5 to 25 ppm and the raw NTU is 3 to 20. Usage of low molecular weight Epi-DMA (being 50% active) is normally 3 to 5 ppm and usage of aluminum chlorohydrate (being 50% active) is normally 20 to 35 ppm. Final water production is normally less than 0.3 NTU. Color is not measured.

High molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active) was used in concert with aluminum chlorohydrate of Applicant (referred to as CV 1120 and being 50% active). Where normal plan operation and the jar tests showed current operation to require 30 ppm of aluminum chlorohydrate in concert with 3 ppm of low molecular weight Epi-DMA, the new chemistry only required 20 ppm of CV 1120 in concert with 2 ppm of CV 3650. The old chemistry only obtained 0.7 NTU at about 40% greater chemical cost.

EXAMPLE 13

In Mena, Arkansas, alum is used in concert with an anionic polyacrylamide in a solids contact clarification system. Typical raw alkalinity values are 3 to 20 ppm and the raw NTU is 3 to 10. Alum usage is normally 40 to 60 ppm along with an excess of 20 ppm of 50% caustic in combination with 10 to 20 ppm of lime. The plant normally produces less than 0.3 NTU.

High molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active) was used in concert with aluminum chlorohydrate (referred to as CV 1120 and being 50% active). Where normal plant operation and the jar tests showed current operation to require 40 ppm of alum, the new chemistry only required 4 ppm of CV 1120 (50% active aluminum chlorohydrate) in concert with 1.5 ppm of CV 3650 (20% active DADMAC at 2,000 cps). The new chemistry obtained 0.7 NTU in the jar test while the old chemistry only obtained 1.0 NTU at about 70% greater chemical cost. At this facility, it is very difficult to obtain a floc at all due to the combination of low alkalinity and low NTU. Therefore, large amounts of alum are normally required. However, CV 1120 and CV 3650 were able to develop a floc easily. Further testing with low molecular weight Epi-DMA (of a molecular weight of 100,000) or low molecular weight DADMAC (of a molecular weight of 200,000) showed no ability to develop a floc and clean the water.

EXAMPLE 14

In Palestine, Texas, alum is used alone in a sedimentation basin system. Typical raw alkalinity values are 20 to 50 ppm and the raw NTU is 5 to 30. The plant normally produces less than 0.1 NTU.

In jar tests, an optimum alum NTU of 0.7 was obtained. By augmenting the jar tests with 1 ppm of high molecular weight DADMAC of Applicant (referred to as CV 3670, having a molecular weight greater than 1 million and being 10% active), the alum dosage was reduced by 40% while 0.6 NTU water was produced.

EXAMPLE 15

In DeQueen, Arkansas, the municipal wastewater plant performs nitrification in a 40 acre pond system. From 3 to 5 times per year, this pond system has an algal bloom of blue/green algae. Blue/green algae emit a nitrogen containing polymer that is toxic to nitrifying microorganisms. Therefore, during periods of blue/green algae blooming, the plant loses its

ability to nitrify, producing water laden with ammonia that is in excess of state and federal permit values.

Testing performed with high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active at 2,000 cps), in combination with Diurion (dichloro-dimethyl-phenolurea manufactured by Dupont) provided that this chemistry blend will flocculate and kill the algae while not harming the nitrosomonas or the nitrobacters. The blend put together was CV 3670 (a high molecular weight DADMAC produced by Applicant, having a molecular weight greater than 1 million and being 10% active at 200 cps) with 10 percent Diurion added by weight.

Two tests were set up: one to measure algal killing performance and one to measure nitrification effectiveness with the product blend. In each test there was a control, one container having 10 ppm of the blend and one container having 25 ppm of the blend. To test for algal growth, water samples were placed in three 5 gallon buckets. To test nitrification, water samples were placed in three 1000 ml beakers. In the beakers, nitrification performance compared to the QC Specification for CV Bio 3010XS (a blend of nitrifiers comprising nitrosomonas and nitrobacters) which is 500 mg of ammonia removed per hour per liter of nitrifiers at 100° F. For the three beakers, variance was well within testing and measurement capabilities (480 mg to 520 mg of ammonia removed/hr/liter of nitrifier). For the three 5 gallon buckets, there was complete algal kills at both 10 and 25 ppm. The control bucket had a flourishing algal bloom throughout the test. It is worth noting that at 25 ppm, the algae was flocculated as well as it was killed.

EXAMPLE 16

In Beaumont, Texas, alum is used in a French Pulsation Clarification System. Typical values are between 20 ppm and 25 ppm of raw alkalinity, 8 ppm of calcium, raw water turbidity units (NTU) of 40 to 60 and raw color of 40 to 80 units. Alum usage is normally 45 to 55 ppm at raw color units of 40 to 60. An anionic polyacrylamide is used in emulsion form at a dosage of 0.2 to 0.4 ppm to control pin floc carryover and floc size. As the raw color units rise, the alum usage increases such that at raw color units of 120 the alum usage is 90 to 100 ppm. The

city of Beaumont normally utilizes 30 to 40 ppm of 50% caustic for pH adjustment, along with 55 ppm of caustic to pH adjust the alum sludge which would otherwise corrode the sewer line.

During numerous jar tests, a combination of aluminum chlorohydrate of Applicant (referred to as CV 1120 and being 50% active), high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active) and aluminum chloride (referred to as CV 1135 and being 10% active). The blend comprises 40% CV 1120, 30% CV 1135 and 30% 3650. Utilizing this chemistry, dosages of 18 to 22 ppm obtained a final 1 micron filtered NTU of 0.2 to 0.8.

EXAMPLE 17

In Nederland, Texas, PRC 3050C is used in a solids contact clarification system. Typical low alkalinity values are between 0 ppm and 30 ppm. Polymer usage is very dependent on the raw color which can vary from 20 to over 300. Polymer usage varies from about 15 ppm to over 70 ppm. Final NTU is normally less than 0.10.

On this day operation was 32 ppm of PRC 3050C. The raw water was 45 NTU. Color was not measured. Visually, one could estimate a color of 50 to 75 standard color units. A blend of aluminum chlorohydrate of Applicant (referred to as CV 1120 and being 50% active), high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active) was prepared for a settled jar test. The preferred embodiment enclosed a blend of 60% CV 1120 and 40% CV 3650. At concentrations of 24 to 28 ppm, NTU's of 0.4 to 0.7 were obtained.

On the same day, a blend of aluminum chlorohydrate of Applicant (referred to as CV 1120 and being 50% active), high molecular weight DADMAC of Applicant (referred to as CV 3650, having a molecular weight greater than 1 million and being 20% active) and aluminum chloride (referred to as CV 1135 and being 10% active) was prepared. This combination produced a blend of 40% CV 1120, 20% 1135 and 40% CV 3650. In a settled jar test, NTU's of 0.6 were obtained at dosages of 28 to 36 ppm.

EXAMPLE 18

Marshall is currently in production with CV 1703. Prior to using CV 1703, Marshall utilized CV 3650 in concert with alum. Alum was used at 30 to 35 ppm along with CV 3650 at 1.5 ppm.

Marshall's raw water quality makes production difficult. At best:

- The raw alkalinity is less than 20 ppm and often as low as 6 ppm,
- The raw turbidity is 2 to 7 NTU,
- The raw color varies from 40 to 300 Standard Color Units, and
- The raw TOC ranges from a UV absorbency of 0.2 to 0.7 m⁻¹, and 5 to 20 ppm.

Prior to the use of CV 3650 with alum, Marshall operated with just alum and often went out of permit having a filtered water turbidity greater than 0.5 NTU. CV 3650 in conjunction with alum improved operation significantly. However, at raw color values over 200 Standard Color Units, Marshall still had difficulties.

Prior to using CV 1703, Marshall produced filtered water at a turbidity of 0.15 to 0.30 NTU under normal conditions and higher when color is a challenge. Since operation with CV 1703, Marshall has kept the filtered water turbidity under 0.08 NTU under all conditions. The settled water turbidity normally varies from 0.01 to 0.07 NTU. Marshall is obtaining 50 to 80% TOC removal with CV 1703.

EXAMPLE 19

Center has a small facility, Mill Creek, that produces 1 to 2 MGD. This facility is over 60 years old and has antiquated equipment in combination with very difficult-to-treat water.

The raw water quality:

- Varies in alkalinity from 10 to 25 ppm,
- Varies in turbidity from 15 to 80 NTU, and
- Varies in color from 30 to 400 Standard Color Units.

Due to inadequate final water quality, during periods of high color, Center would shut this facility down. During normal operation, Center had to pre-chlorinate to produce filtered

water with a turbidity of less than 0.2 NTU. Previous to usage of CV1703, the settled water turbidities were 3 to 4.5 NTU.

Since operation with CV1703, Center normally produces settled water turbidity of less than 1.0 NTU and always less than 1.5 NTU. Center has been able to stop pre-chlorination, producing filtered water with a turbidity of less than 0.1 NTU and has successfully treated water with a raw color of 400 Standard Color Units.

EXAMPLE 20

Nacogdoches has raw water with:

- An alkalinity of 10 to 25 ppm,
- A turbidity of 4 to 20 NTU, and
- Color of 10 to 100 Standard Color Units.

Nacogdoches normally operates using 25 to 40 ppm of alum. During periods of the raw color exceeding 70 Standard Color Units, Nacogdoches will operate at near or slightly exceed permit.

A plant evaluation utilizing CV1735 was held on 6/20 to 23/99. During this evaluation the water quality was:

- A raw water alkalinity of 18 ppm,
- A raw water turbidity of 24 NTU,
- A raw water color of 56 Standard Color Units,
- A settled water turbidity of 0.7 NTU,
- A filtered water turbidity of 0.1 to 0.15 NTU, and
- A filtered water color of 7 Standard color units.

During the evaluation, Nacogdoches operated at:

- A settled water turbidity of 0.4 to 0.6 NTU,
- A filtered water turbidity of 0.10 NTU,
- A final color of "0" Standard Color Units, and
- A dosage of 5 ppm of CV1735.

EXAMPLE 21

5 In Beaumont, Texas, alum is used in a Pulsation Clarification System. Typical raw water values are between 20 ppm and 25 ppm of raw alkalinity, 8 ppm of calcium, and 40 to 60 NTU. An anionic polyacrylamide is used in emulsion form at a dosage of 0.2 to 0.4 ppm to control pin floc carryover and floc size. As the raw color units rise, the alum usage increases such that at raw color units of 120 the alum usage is 90 to 100 ppm. The City of Beaumont normally utilizes 30 to 40 ppm of 50% caustic for water pH adjustment along with 55 ppm of caustic to pH adjust ^{the} alum sludge, which would otherwise corrode the sewer line.

10 During numerous jar tests, CV 1730, a combination of 25 volume percent $Al_xOH_yCl_z$ being 50% active and 84% basic (CV 1120), 30 volume percent aluminum chloride being 10% Al_2O_3 (CV 1135), 30 volume percent Epi-DMA 50% active at 120 cps (CV 3210) and 15 volume percent DADMAC 20% active at 2,000 cps. CV 1730 was used with CV 6230P, a 40% active emulsion of 30% anionic polyacrylamide. CV 1730 was compared in jar tests without CV 6230 P.

15 In addition, CV 1120 was tested in combination with CV 3210 and CV 3650. These tests were repeated and without CV 6230P. The jar testing sequence utilized was that normally practiced by the City of Beaumont. Results showed best results on the dosage curve to be:

20 1.A. Utilizing CV 1730 at 40 ppm in concert with CV 6230P at 0.4 ppm, resulted in a final NTU of 0.15 in combination with 5 Standard Color Units.

21 1.B Utilizing CV 1703 at 40 ppm without CV 6230P, resulted in a final NTU of 3.1 in combination with 14 Standard Color Units.

22 2.A Utilizing CV 1120 and CV 3210 in a mass ratio of 20:1 at 60 ppm with 0.4 ppm of CV 6230 P, resulted in a filtered NTU of 0.30 with 13 Standard Color Units.

25 2.B Utilizing CV 1120 and CV 3210 in a mass ratio of 20:1 at 45 ppm without CV 6230 P, resulted in a filtered NTU with 12.1 with 9 Standard Color Units.

3.A Utilizing CV 1120 and CV 3650 in a mass ratio of 20:1 at 60 ppm with 0.4 ppm of CV 6230 P, resulted in a filtered NTU of 0.05 with 7 Standard Color Units.

3.B Utilizing CV 1120 and CV 3650 in a mass ratio of 20:1 at 45 ppm without CV 6230 P, resulted in a filtered NTU of 9.3 with 15 Standard Color Units.

EXAMPLE 22

The City of Marshall is currently in production with CV 1703. Marshall's new water quality makes production difficult with salt chemistry:

- The raw alkalinity is less than 20 ppm and often as low as 6 ppm,
- The raw turbidity is 2 to 11 NTU,
- The raw color varies from 40 to 300 Standard Color Units, and
- The raw TOC range from 6 to 20 ppm.

Since the City of Marshall was the first to utilize this chemistry on a production basis, the use of Cationic Polyacrylamides to replace high molecular weight DADMAC was jar tested. The results were very positive. Two sets of jar tests were performed. The jar test sequence is that normally utilized by the City of Marshall. The first set was performed with the current CV 1703 formulation referenced in Figure 10. The second set was performed utilizing the same volume ratios in CV 1703 of $Al_xOH_yCl_z$, $AlCl_3$, and low molecular weight Epi-DMA, however, the 10 percent by volume high molecular weight DADMAC was replaced with 5 percent by volume CV 5180. The remaining 5% of the 1903 formulation was water. CV 5180 is an 80% cationic polyacrylamide having a molecular weight near 8 million. This blend utilizing the CV 5180 is labeled CV 1903.

The raw water quality on 4/5/00 was 9.2 NTU with 160 Color Units. The best results of the two jar tests performance curves are:

- A dosage of 35 ppm of CV 1703 resulting in a settled NTU of 0.98 and 13 Standard Color Units.
- A dosage of 35 ppm of CV 1903 resulting in a settled NTU of 0.72 and 13 Standard Color Units.

EXAMPLE 23

The City of Port Arthur, Texas operates a Pulsator Clarifier. Raw water quality varies from approximately 5 ppm to approximately 40 ppm of alkalinity, from approximately 10 to 100 NTU and from approximately 20 to 150 Standard Color Units. Jar tests were performed

with CV 1756 resulting in less than 1.0 NTU and less than 5 Standard Color Units on many occasions during 1998 and 1999. CV 1756 is on a volume basis 65 to 68% of CV 1120, 25 to 30% CV 3210 and 7.5 to 10% CV 3250. CV 3250 is a 50% active high molecular weight Epi-DMA.

5 In November of 1999, Port Arthur was operating the Pulsator on alum with a low molecular weight DADMAC. Tests had been performed with alum and a medium molecular weight DADMAC achieving mixed results. At this time, plant performance with alum and DADMAC was not optimal; often the final NTU was in excess of 0.5. Upon plant start-up in November of 1999, the CV 1756 alone allowed floc to carry over the weirs. Jar tests were performed replacing the high molecular weight Epi-DMA in the CV 1756 formulation with high molecular weight DADMAC. The results were not as good as the Epi-DMA. Therefore, jar tests were performed using CV 5140 (cationic) and CV 6200 P (non-ionic) and CV 6230 P (anionic) polyacrylamides. Where good results were obtained with CV 5140 and CV 6230 P, the best results were obtained with CV 6200 P. Cytec 1986 (non-ionic polyacrylamide) was on site and performed nearly equivalent to CV 6200 P; therefore, Cytec 1986 was put into production with CV 1756.

Plant operation with CV 1756 and Cytec 1986 produced equivalent results to those of the jar tests. The raw water quality was approximately 25 to approximately 35 NTU with 25 to 40 Standard Color Units. CV 1756 operated at 15 to 18 mg/L and Cytec 1986 operated at a dosage of 0.2 to 0.45 mg/L. Weir NTU dropped from 3 to 5 NTU to less than 1.5 NTU and often to less than 1.0 NTU; the filtered NTU dropped to less than 0.15 NTU. Later in the plant evaluation, high winds caused waves in the clarifier; these winds were the reason for the Cytec 1986 increases to 0.45 mg/L.

25 EXAMPLE 24

The City of Shreveport, LA produces water with a traditional settling basin clarifier. Raw water alkalinity varies from approximately 10 ppm to approximately 40 ppm, turbidity varies from approximately 10 to approximately 45 NTU and color varies from approximately 30 to over 150 Standard Color Units.

CV 1795 was jar test evaluated to be the optimum combination for this water. The jar testing sequence utilized is that utilized by the City of Shreveport. CV 1795 is by volume 45% CV 1120, 15% CV 3250 (high molecular weight Epi-DMA being 8,000 cps at 50% active), 30% CV 3210 and 10% water/ CV 1795 was then compared to CV 1995. CV 1995 has the same ratios as CV 1795, except the CV 3250 is replaced with 5% of CV 5180 (80% cationic polyacrylamide which is a 40% active emulsion). The remaining 10 percent of the CV 1995 formulation is water. The results of CV 1795 and CV 1995 were very comparable.

On 4/6/00, the raw water quality in Shreveport was 13.1 NTU and 146 Color Units. Jar testing with CV 1795 produced 0.47 NTU and 8 Color Units at 9 ppm. Jar testing with CV 1995 produced 0.53 NTU and 8 Color Units at 9 ppm.

EXAMPLE 25

The City of Marshall is currently in production with CV 1703. Marshall's raw water quality makes production difficult with salt chemistry.

- The raw alkalinity is less than 20 ppm and often as low as 6 ppm,
- The raw turbidity is 2 to 11 NTU,
- The raw color varies from 40 to 300 Standard Color Units, and
- The raw TOC ranges from 6 to 20 ppm.

Since the City of Marshall was the first to utilize this chemistry on a production basis, the importance of the molecular weight of the DADMAC is tested in Marshall. Three sets of jar tests were performed. The jar test sequence is that normally utilized by the City of Marshall. The first set was performed with the current CV 1703 formulation referenced in Figure 10. The second set was performed utilizing the same volume ratios in CV 1703 replacing the high molecular weight DADMAC (CV 3650) measuring 2,000 cps at 20% active with a low molecular weight DADMAC measuring 200 cps at 20% active. The third set was performed replacing CV 3650 with a medium molecular weight DADMAC measuring 780 CPS at 20% active.

The raw water quality on 5/14/99 was 12 NTU with 184 Color Units. The best results of the three jar test performance curves are:

- A dosage of 28 ppm of CV 1703 "HMW DADMAC" resulting in a settled NTU of 0.72 and 8 Standard Color Units.
- A dosage of 32 ppm of CV 1703 "LMW DADMAC" resulting in a settled NTU of 2.31 and 34 Standard Color Units.
- A dosage of 30 ppm of CV 1703 "MMW DADMAC" resulting in a settled NTU of 1.10 and 18 Standard Color Units.

The test results suggest that in waters where a HMW AmP performs very well, a MMW AmP may perform substantially equivalently, or at least well enough to meet targeted standards.

EXAMPLE 26

In Marshall, Texas CV 1703 has been documented to remove TOC down to the DOC level. To enhance DOC removal, many reformulations of CV 1703 were evaluated producing no improvement in DOC removal. Further, in combination with CV 1703, KMnO₄ and KMnO₄ with Powdered Activated Carbon were evaluated; there was no improvement in DOC removal. Finally, alum was evaluated in combination with KMnO₄ and KMnO₄ with Powdered Activated Carbon; in this case, there was a slight improvement in DOC removal, however, not enough to allow Marshall to remove enough of the DOC.

Since alum had a slight improvement over that of CV 1703 in removing DOC, it was theorized to use the new sulfated versions of $Al_xOH_yCl_z$. This theory was based on the sulfate anion combining with DOC by nucleophilic substitution, thereby allowing coagulation. Where the sulfated versions of $Al_xOH_yCl_z$ in CV 1703 performed equivalently on a % Al₂O₃ basis as compared to CV 1120 in CV 1703, there was no improvement in DOC removal.

Further bench tests in Marshall with CV 1787 and CV 1703 reveal maximal Aluminum concentrations in the clarified water of 0.15 mg/L with most results non-detect by a Hach DR 2000. Actual production results measured by the TNRCC reveal a maximum aluminum concentration in the final water of 0.05 mg/L, with most results non-detect.

EXAMPLE 27

The City of Hot Springs, AR produces water from Lake Quachita. The raw water quality is low alkalinity with low turbidity. Lake Quachita does not measure any appreciable color in the water. Raw water alkalinity varies from about 10 to 30 ppm, NTU varies from about 10 to 30 ppm.

CV 1787 was tested in Hot Springs at the Quachita Facility. CV 1787 is by volume 85% CV 1120 (50% active, 84% basic $Al_xOH_yCl_z$) and 15% CV 3250 (HMW Epi-DMA measuring 9,000 cps at 50% active). CV 1787 was compared to a version replacing CV 3250 with CV 3210 which is a low molecular weight Epi-DMA measuring 120 cps at 50% active. A third test was performed replacing CV 3250 in the CV 1787 formulation with a medium molecular weight Epi-DMA, CV 3230. CV 3230 measures approximately 3,500 cps at 50% active.

On 3/31/99 the raw water quality was 20 ppm of alkalinity and 2.5 NTU. The best results of the dosage curves were:

- A dosage of 6 ppm of CV 1787 "HMW Epi-DMA: resulting in a settled NTU of 0.7.
- A dosage of 5 ppm of CV 1787 "LMW Epi-DMA: resulting in a settled NTU of 1.9.
- A dosage of 6 ppm of CV 1787 "MMW Epi-DMA: resulting in a settled NTU of 1.1.

The example suggests that in waters where a HMW AmP performs very well, a MMW AmP may perform substantially equivalently, or at least well enough to meet targeted standards.

EXAMPLE 28

The City of Arlington, Texas produces municipal water from two plants, the Pierce Burch (PB) and the John Kabala (JK) plants. Arlington has installed ozonation facilities at each. The coagulation chemicals at each are currently alum in concert with a low molecular weight DADMAC. Where the pre-ozonation provides micro-flocculation to enhance the effectiveness of the alum, the resulting floc is rather small. The filter loadings at both facilities are so significant that filter run times are often less than 20 hours.

At the PB Plant, CV 1754 and CV 1788 were found to produce water at less than 1.0 settled NTU at dosages of less than 8 mg/L while the plant was operating at 0.8 mg/L of ozone

pre-treatment with 25 mg/L of alum and 1.1 mg/L of low molecular weight 40% active DADMAC. CV 1754 is by volume 70% CV 1120 (50% active, 84% basicity ACH), 10% CV 3650 (high molecular weight DADMAC being 2,000 cps at 20% active) and 20% CV 3250 (high molecular weight Epi-DMA being 8,000 cps at 50% active). CV 1788 is by volume 80% CV 1120, 10% CV 3650 and 10% CV 3210 (low molecular weight Epi-DMA being 100 cps at 50% active).

At the PB Plant, where CV 1788 performed very well in the non-ozonated water, the performance was not acceptable in the pre-ozonated water. In contrast, the CV 1754 performed very well in the water with 0.8 mg/L of pre-ozonation; in that water CV 1754 produced a settled NTU of 0.95 at 8 mg/L. During this period, filter hours were less than 20. On this day an additional test was performed with a compound that included cationic polyacrylamide. This tested combination, CV 1901 is by volume 90% CV 1120, 6% CV 5160 (a 60% cationic polyacrylamide being 40% active in a mineral oil emulsion) and 4% water. CV 1901 produced a settled NTU of 0.91 at 8.0 mg/L in 0.8 mg/L pre-ozonated water and produced a settled NTU of 0.88 at 6.5 mg/L in non-ozonated.

At the JK plant, tests with water pre-ozonated showed CV 1780 to perform at 0.6 settled NTU at 3 mg/L; JK normally operates with 10 mg/L of Alum in concert with 1.0 mg/L of a 40% active low molecular weight DADMAC producing a settled NTU of approximately 1.0 NTU. CV 1780 is by volume 50% CV 1120 and 50% CV 3650. These tests showed the ozonated water to be very sensitive to the amount of CV 3650; a 40/60 ratio could not obtain less than 1.0 NTU.

CV 1754 will save more in operating cost than the PB Plant will spend on the chemical; operating savings are estimated to be near \$350,000 per year above the chemical purchases with chemical purchases estimated to be near \$180,000 per year. CV 1780 will also save more in operating cost than the JK Plant will spend on the chemical; operating savings are estimated to be near \$170,000 per year above the chemical purchases with the chemical purchases estimated to be near \$130,000 per year.

EXAMPLE 29

The City of Springfield, MO produces municipal water from three water production plants. Where raw water turbidity spikes can run as high as 50 NTU, the normal raw NTU is less than 5 with the raw alkalinity normally over 100 mg/L; there is no measurable color.

The current chemical treatment program is with General 4090, a 50% active 70% basic aluminum hydroxylchloride. The current dosage is near 8 mg/L with the settled NTU near 0.3 NTU. Jar testing with CV 1745 (70% by volume CV 1120 (50% active 84% basic aluminum chlorohydrate), 20% by volume CV 3650 (20% active DADMAC being 2,000 cps) and 10% by volume CV 3210 (50% active Epi-DMA being 100 cps) or CV 3620 (40% active DADMAC being 100 cps). CV 1785 (90% CV 1120, 2.5% CV 3250 and 7.5% CV 3210 and CV 1788 (80% CV 1120, 10% CV 3650 and 10% CV 3210) produced settled NTU's of less than 0.5 NTU at dosages of less than 4 mg/L.

EXAMPLE 30

The City of Kansas City, MO operates a 210 MGD lime softening facility normally producing water with less than 0.1 NTU and less than 80 mg/L of hardness.

During the winter months cold temperatures do not allow the lime to flocculate properly producing settled water in the final basins from 10 to over 20 NTU. In addition, the Spring rains cause the same challenge with respect to final turbidity performance producing a final settled NTU of 5 to over 20.

Jar tests were performed utilizing CV 1788 which is by volume 80% CV 1120 (50% active aluminum chlorohydrate that is 84% basic). 10% CV 3210 (50% active Epi-DMA measuring 100 cps) and 10% CV 3650 (20% active DADMAC measuring 2,000 cps). At dosages of 1 to 3 m/L settled NTU's of less than 1.0 were achieved.

EXAMPLE 31

The City of DeQueen, AR has low alkalinity/low - moderate turbidity raw water that has a minimum of 4 mg/L of mineral salts. Due to the concentration of mineral salts in the water, it has been found that the medium, high and very high AmP's are not required for water

clarification. It is believed that the mineral content of this raw water causes this raw water to perform uniquely. Further, AP's and AS's in concert with low molecular weight quaternary ammonium compounds perform very poorly.

However, where the combination of an AP alone will perform satisfactorily, an AP with an AS or an AP with an AS and with a low molecular weight quaternary ammonium polymer perform excellently. NTU results for this testing is:

Product	Dosage	Settled NTU
CV 1787	13	> 3.0 NTU
CV 1120	13	0.93
CV 1170	13	0.25
CV 1180	13	0.34
CV 1190	13	1.1

EXAMPLE 32

During the summer of 2000, two bulk storage tanks formed an agglomeration of Aluminum Hydroxide intermixed with AmP. The product in both cases was CV 1703. Upon investigation, the cause of this precipitate agglomeration was evaporation of water from the blended AP/AmP solution. This was determined by residual sodium analysis. The mg/L of sodium in both cases doubled from nearly 400 mg/L to nearly 800 mg/L; in addition, the CV 1703 thickened significantly before forming the precipitated agglomeration.

Further investigation found other Aluminum compounds to have the same challenge. Beakers of Alum, Aluminum Chloride and Aluminum Chlorohydrate were left open in direct sunlight. All formed Aluminum Hydroxide precipitates when the solubility point was crossed due to water evaporation.

As a result of this work, all customers of this technology are recommended to install nitrogen blanket/vent systems to insure that the product does not form a precipitate, thereby remaining stable.

FURTHER TEST RESULTS

Figures 3-8 show the results of testing of various processes of the present invention in raw water of various alkalinities and turbidities. As used in these Figures, the stated TOC values are proportional to the UV-254 measurements. Unless otherwise specified, any measurements of TOC provided are the actual UV-254 measurements in units of m^{-1} .

Figure 3 refers to test results that were obtained for the section "A" shown in Figure 1 in raw waters of low alkalinity and low turbidity. As is demonstrated in Figure 3, the alkalinities of the raw water ranged from between 8 ppm to 26 ppm and the turbidity ranged from between 1 NTU and 16 NTU (except one case in test 12 in which the turbidity of the raw water was 23 NTU). The resulting settled water turbidities ranged between 0.2 NTU and 0.9 NTU which are lower than the maximum turbidity requirements established by the government. The only case where the required turbidity for the settled water was not achieved was in test 3. Settled water turbidity of 1.2 NTU was achieved due to the fact that the jar tests were designed to match the plant capabilities. The plant in Center, Texas, had very poor mixing facilities. With plant modification, the operation of the plant provides settled water turbidity results of less than 1.0 NTU. Also, the color content of the raw water ranged between 37 and 260 Standard Color Units. The settled water had a color content ranging from 0 to 18 Standard Color Units. Only in two cases, the settled water color content was over the 15 Standard Color Units requirement of the government. In test 6 and 9, the color content of the settled water was 18 and 17 Standard Color Units, respectively. However, it is well known in the art that anthracite filters can easily remove 5 Standard Color Units. Therefore, by using anthracite filters in those two cases, the achieved color content of the settled water shall be below 15 Standard Color Units, as required by the government. Also, as shown on page 9, the required removal of TOC by enhanced coagulation and softening has to be at least 35.0% in a raw water of an alkalinity of at most 60 ppm and TOC of greater than 2.0 and up to 4.0 ppm. As demonstrated in Figure 3, only in tests 7 and 8 the TOC was measured at UV-254 measurement of 0.40 and 0.29 m^{-1} , respectively. Upon treatment of the raw water, the settled water had no TOC after performance of the inventor's test. In test 8, the TOC as measured by UV-254 of the raw water was reduced from 0.29 to 0.08 m^{-1} , which is a reduction of approximately 70%, thus satisfying the required

removal of TOC established by the government. In test 11, upon using CV1710, a 47% TOC removal was obtained, while by using alum alone TOC removal of only 19% was achieved. Of course, it should be noted that all results obtained in the tables refer to the best results on curves that were obtained after treating the raw waters, as is commonly practiced in the industry.

Figure 4 reflects the results that were obtained for treating low alkalinity, and moderate and high turbidity raw water. Again, Figure 4 reflects that all the results that were obtained upon applying the claimed combinations were capable of achieving the required government standards of turbidity, color content and TOC removal. It should be noted that tests 2 and 3 are only using one-component chemicals. In test 2, aluminum chlorohydrate is used. In test 3, aluminum chloride is used. In those two tests, the turbidity of the settled water was 5.6 NTU and 10.2 NTU, demonstrating that one-component systems do not perform the results achieved by the claimed invention. However, upon application of the compounds that are claimed by the applicant, the settled water turbidity results that were obtained ranged between 0.1 NTU and 0.9 NTU, which are all acceptable by the present government standards for settled turbidity. Regarding color, all tests that measured color content of the raw water and the settled water provided extraordinary results. In test 5, the raw water had a color content of 225 Standard Color Units, yet the settled water had a color content of 6 Standard Color Units which satisfies the maximum of 15 Standard Color Units set by the government. Similarly in tests 6, 7, 8 and 10, color content of the raw water (150, 128, 42 and 108 Standard Color Units) was reduced to under 15 Standard Color Units (i.e., 10, 7, 2 and 5 Standard Color Units). Only in test 9 was the color content of the settled waste over 15 (i.e., 16) Standard Color Units. However, in this case the raw water was spiked with tannic acid for capability testing, and in addition the color content can always be removed up to 5 Standard Color Units upon using anthracite filters (as specified for Figure 3). In Figure 4, TOC measurements were not considered.

Figure 5 relates to section C of Figure 1, with the raw water having a low alkalinity, and low, moderate and high turbidity. The tests of Figure 5 were run in raw waters having a turbidity of 8 NTU and 38 NTU and an alkalinity of 44 ppm and 40 ppm, respectively. The resulting turbidity of the settled water in both cases was reduced to below 1.0 NTU (i.e., 0.9 NTU and 0.8 NTU). The color content in test 2 was reduced from 98 Standard Color Units in

the raw water to 9 Standard Color Units in the settled water, satisfying present government standards. There was no measurement of the TOC removal in Figure 5.

Figure 6 corresponds to section D of Figure 1, having a moderate and high alkalinity, and moderate and high turbidity. In all the tests listed in Figure 6, the turbidity of the settled water was below 1.0 NTU, ranging between 0.1 NTU and 0.9 NTU. It should be noted that the raw water turbidity ranged from 20 NTU to 27 NTU. As is clearly indicated in Figure 6, the raw water alkalinities of the test ranged between 81 ppm and 150 ppm, qualifying the water as a raw water with moderate and high alkalinity. The color content of the raw water was not visible and therefore was not treated. However, the TOC was treated. In test 4, the TOC of the raw water was 0.079 m^{-1} , while it was 0.05 m^{-1} in the settled water approximating 36% removal. As shown in the table for required removal of TOC, the required TOC removal is even below 35.0% for high alkalinity and moderate alkalinity waters (less than 35.0%). In test 5, the TOC of the raw water was 0.261 m^{-1} , while the TOC of the settled water was 0.06 m^{-1} , showing an approximate removal of TOC by over 75%.

Figure 7 represents the results that were obtained at moderate and high alkalinities and low turbidity raw waters, as demonstrated in Section E of Figure 1. All the turbidity results were under 1.0 NTU. The turbidity of the raw water ranged between 4 NTU and 16 NTU, while the turbidity of the settled water ranged between 0.1 NTU and 0.7 NTU. Since there was no detectable color content, no results are listed in reference to the color content of the raw water or the settled water. Meanwhile, there was no TOC listing on Figure 7. Although a portion of Section E of Figure 1 (i.e., alkalinities ranging from 50 to 150 ppm) and low turbidities were demonstrated in Hassick, none of the results provided by Hassick ever achieved turbidity of under 1.0 NTU which is required by the present government standards. It should also be noted that Section C does not have any upper limits on its turbidity range (as demonstrated by the continuous arrow on the right side of the graph). Similarly, Section D does not have a limitation of high turbidity and at the present, the same chemical compounds have worked in numerous raw waters of various turbidities. Similarly, there is no upper limits on the high alkalinity range of Section E.

In Figure 8, numerous other features that are important in the present application are shown. The molecular weight of the AmP does make a difference in the results. Comparison of test 1 with test 2 of Figure 8 shows that when low molecular weight DADMAC was used, the resulting settled water turbidity was 2.4 NTU, while when high molecular weight DADMAC was used in the chemical compound, a turbidity of 0.7 NTU was obtained for the settled water upon using the exact same raw water.

Test 3 and test 4 of Figure 8 can also be compared to show the effect of molecular weight of the AmP on the results. Using high molecular weight DADMAC and aluminum chloride alone provided a resulting turbidity of 1.1 NTU, while under the exact same conditions, using aluminum chloride with low molecular weight DADMAC provided a turbidity of 2.1 NTU for the settled water. In test 5-7 of Figure 8, the use of poly-aluminum chloride alone provided a turbidity of 1.6 NTU for the settled water while the use of aluminum chloride alone provided a turbidity result of 0.4 NTU for the settled water. However, as stated before, higher dosages of aluminum compounds are not desired for treating settled water. Under the exact same conditions, a settled water turbidity of 0.3 NTU was obtained (refer to test 7). Similarly in tests 8 to 10, the results that were obtained by using the chemical compound resulted in a settled water turbidity of 0.3 NTU, while under the same conditions poly-aluminum chlorohydrate and aluminum chloride each provided a turbidity of 3.5 NTU and 1.1 NTU, respectively. Tests 11 to 13 of Figure 8 are very similar and indicate again that the compound performs even much better than the single components themselves do, achieving a settled water turbidity of 0.7 NTU versus achieving turbidities of 2.8 and 6.0 NTU in the settled water. It should also be noted that using low molecular weight quaternized ammonium polymers (versus medium, high and/or very high AmP) does not even provide satisfactory results regarding color content, with test 1 to 4 of Figure 8 showing that color content of 8 and 13 Standard Color Units were obtained when high molecular weight AmP's are used while a color content of 34 and 27 Standard Color Units were obtained when low molecular weight quaternary ammonium polymers were used.

The test results prove that the combinations claimed by the applicant are capable of achieving the required government standards of TOC removal, specifically the insoluble component (IOC), non-DOC component, in raw waters of:

- (a) alkalinity of less than 30 ppm and turbidity of less than 20 NTU (as shown by Section A of Figure 1);
- (b) alkalinity of less than 30 ppm and turbidity of between 20 NTU and 150 NTU (as shown by Section B of Figure 1);
- (c) alkalinity of between 30 ppm and 50 ppm and any turbidity (as shown by Section C of Figure 1)
- (d) alkalinity of greater than 50 ppm and turbidity of greater than 20 NTU (as shown in Section D of Figure 1); and
- (e) alkalinity of greater than 50 ppm and turbidity of less than 20 NTU (as shown by section E of Figure 1).

It is also inherently obvious that the production of these high and very high molecular weight polymers is more costly than their low molecular weight counterparts due to equipment investment and equipment utilization. AmP's obtain their molecular weight in direct proportion to reactor residence time. Production of organic polymers with high and very high molecular weights requires significantly increased reaction times. Further, production of high and very high molecular weight solution polymers necessitates improvements in equipment due to viscosity increases that occur at molecular weights over 2,000,000. Only in the last 6 years have these equipment restrictions been overcome. Due to these production expenses, industry took many years to address the production technology issues. The high and very high molecular weight AmP's can now be combined with the AP's to create a novel generation of water treatment chemicals.

Certain objects are set forth above and made apparent from the foregoing description, tables, drawings and examples. However, since certain changes may be made in the above description, tables, drawings and examples without departing from the scope of the invention, it is intended that all matters contained in the foregoing description, tables, drawings and examples shall be interpreted as illustrative only of the principles of the invention and not in

a limiting sense. With respect to the above description, tables, drawings and examples then, it is to be realized that any descriptions, tables, drawings and examples deemed readily apparent and obvious to one skilled in the art and all equivalent relationships to those stated in the tables, drawing and examples and described in the specification are intended to be encompassed by the present invention.

Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly, all suitable modifications and equivalents may be resorted to, falling within the scope of the invention. It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall in between.